Rapid Fabrication of Vascular Channel Networks in Composite Materials

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Abstract

Multifunctionality in polymer matrix composites (PMCs) is often stated as a goal to achieve reduced system mass, volume, and complexity. One method for creating a multifunctional material is to fabricate small channels in the PMC, forming a 'vascular' PMC. These channels can be used for circulating a functional fluid, such as a coolant, adhesive, or conductive fluid to achieve temperature regulation, internal damage repair, or electromagnetic modulation, respectively. While vascular PMCs have been well studied in the literature, more work is needed to understand cost effective methods for their fabrication.

In this work, we evaluated the use of sacrificial metal wire preforms incorporated into PMCs to fabricate a series of channels. Accordingly, the wire was placed into the fiber preform, the matrix was introduced and hardened, and the wire was removed by increasing the temperature to melt the metal. The evaluated insertion techniques included manual placement of the wire into the layup and co-braiding of the wire with the structural fibers. The bulk of the melted metal was removed by forcing air through the channels to displace the metal. The effectiveness of room temperature air and elevated temperature air was studied. Also, an optional cleaning step was evaluated that removes the residual metal from the walls of the channels by chemical etching with either HCl solution, $FeCl_3$ solution, or NH_4OH solution. The results showed that the channels can be formed using meltable metal wires while achieving no apparent damage to the PMC, little-to-no residual metal in the channels, and comparable mechanical properties in the resulting PMC to those without channels.

Introduction

Methods for composite channel manufacture are documented in numerous studies throughout the literature [1–4]. Inspiration for vascular composites originates from biological vasculature [5,6]. Plants and mammals for example, rely upon extensive vascular networks to transport fluids and nutrients throughout their structures and perform necessary biological functions [2,7]. Applications for vascular networks in composites include thermal regulation, structural repair, electromagnetic modulation, and damage sensing [4].

Active cooling systems for thermal regulation are critical for battery systems, aerospace components, fuel cells, and various other electronics. Within a vehicle, composite structures can experience temperatures above 150 °C in hot climates or during heavy traffic [8]. Also, heat generating systems, such as battery packs or high-powered electronics, often require a source of thermal regulation [9,10]. Without cooling channels, systems which encounter high temperatures have reduced structural properties and fail more rapidly than parts which contain vascular cooling channels to stabilize the system [11,12]. It is important that the material temperature remains below the glass transition temperature of the polymer. A cooling system integrated into the material itself can reduce system mass, volume, and cost by avoiding the need for expensive high-temperature resistant resins or eliminating external heat exchangers.

The channels or vascular networks can also enable repair [13]. The automotive and aerospace industries have placed a lot of emphasis on repair of PMCs. Channels can help reach regions of the composite which were previously difficult to reach for repair. When a part cracks, healing agents can be injected into the area via an integrated channel network.

Current methods for developing a vasculature system within PMC materials include embedding hollow tubules, removal of solid materials, high voltage electrical discharge, lost “wax” type processes, and vaporization of sacrificial components (VaSC) [14]. Of these methods, the lost “wax” process shows the most promise for automotive production (Figure 1). In this process, a meltable sacrificial preform is embedded into a liquid resin, the resin is hardened, and the preform is melted and removed to create a channel. In this work, we examine the use of a low-melting point metal as the “wax”. Advantages to this process are that the metal can be removed during a normal post-curing process for the PMC, the metal is removed quickly once the required temperature is reached, and the metal is recyclable for forming channels in the next parts.

The objective of this work is to study the process of creating channels with the lost “wax” method using metal wires as a meltable sacrificial material. Various methods were investigated to completely remove the sacrificial material without any remaining residues.

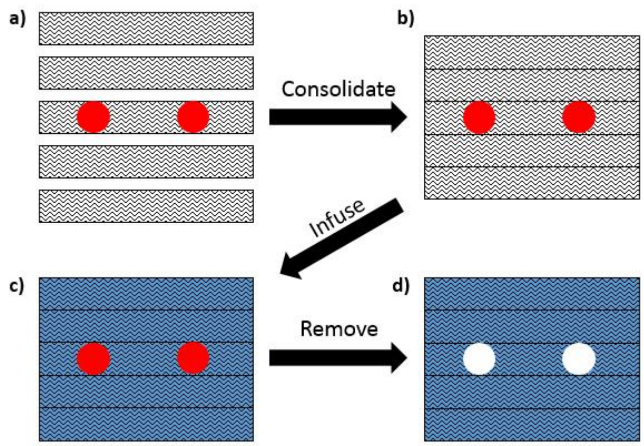


Figure 1: Process for fabricating vascular composites using metal as a sacrificial material. (a) Layers of fabric are stacked, some of which contain the sacrificial material. (b) The layers are consolidated. (c) The fabric is filled with resin and cured. (d) The sacrificial material is removed.

Materials

The sacrificial material used in this study was the eutectic alloy Kappa Aloy9 – 91Sn/9Zn (91% Tin, 9% Zinc) wire from KappAlloy with a 0.5 mm diameter (PN 121-02001) and a melting temperature of 200 °C. Braided composite fabric from A&P Technology was used to generate layered composite plaques both with and without the solder wire channels using a resin composed of DER 383 epoxy (Dow Chemical) & BV-ME-PS2 anhydride hardener (Broadview Chemicals). The plaques were post-cured in a Thermal Product Solutions Blue M convection oven and divided into specimens using a diamond blade wet-saw. An illustration of the fabric can be seen in *Figure 2*.

Materials trialed for removing the sacrificial material once it was encased in the composite plaques include varying concentrations of BDH Hydrochloric Acid, 36.5-38% (CAS:7647-01-0) from VWR Analytical, reagent grade Iron (III) Chloride, 97% (CAS: 7705-08-0) from Sigma Aldrich, Ammonium Hydroxide, 56.6% (CAS:1336-21-6) from Sigma Aldrich. Each was diluted with deionized water.

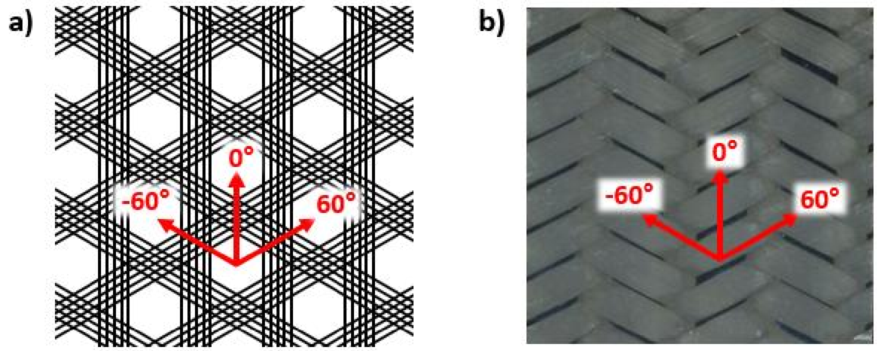


Figure 2: Triaxial braided fabric angular illustrations.

Experimental

Plaque Molding

Composite plaque molding both with and without the sacrificial material channels was completed in an enclosed rectangular mold in a hydraulic press using five layers of triaxial braided fabric infused with resin composed of the epoxy DER 383 and the hardener BV-ME-PS2 anhydride in a mixture ratio by mass of 100:88 respectively. Both components were preheated to 60 °C, mixed by hand, injected directly into the mold set to 130 °C using pressure pot molding, then cured for 20 min under high pressure. The plaques were extracted, left overnight to reach room temperature and post-cured the following day at 170 °C in a convection oven.

The sacrificial materials were placed in the fabric layup approximately 9 mm apart by one of two methods. In the first, the wires were placed by hand and secured using high-temperature tape. Placement between the second and third layer and placement at the top of the fifth layer were compared. In the second method, the sacrificial materials were braided by A&P Technologies directly into the fabric. The third fabric layer in that case contained the solder wires. The differences between method 1 and 2 are shown in Figure 3 below. The final plaque thickness was 2.5-2.7 mm. Each plaque was cut into several specimens using the diamond blade wet saw. The specimens were 36 mm wide and contained 3 sacrificial material channels each.

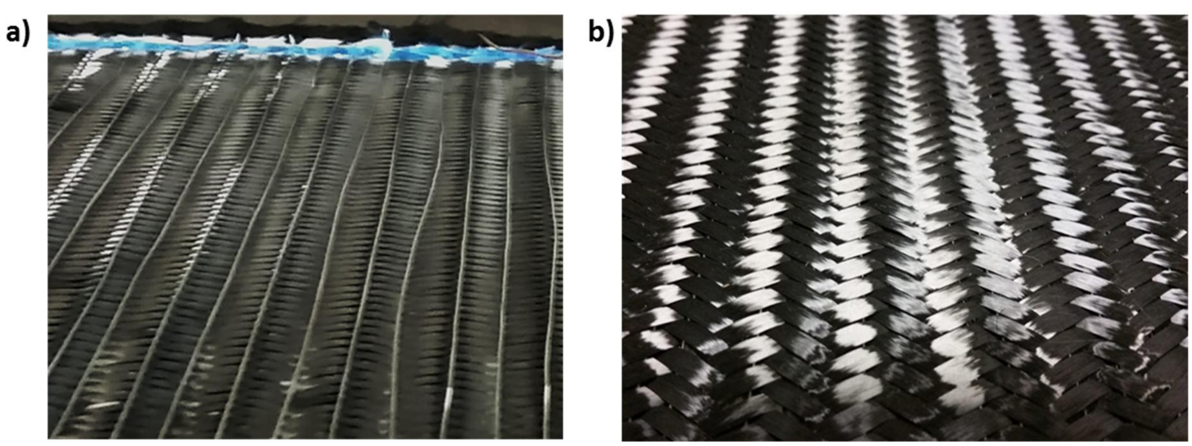


Figure 3: (a) Wire introduced on top of the second fabric layer. (b) Wire introduced directly into the fabric as the third fabric layer was not visible on the surface.

Sacrificial Material Removal & Channel Manufacture

The specimens containing channels were drilled out approximately 3 mm deep to allow for the attachment of a syringe needle. Thermally resistant tubing was attached to the syringe to connect the source of the flushing fluid. The specimens were briefly heated in a convection oven to 205 °C to melt the metal sacrificial material. Then, compressed air was blown through the channels at 40 psi static pressure. Both hot (>200 °C) and room temperature (ca. 22 °C) compressed air temperatures were examined. Figure 4 illustrates the inline heater used to heat the compressed air prior to flushing.

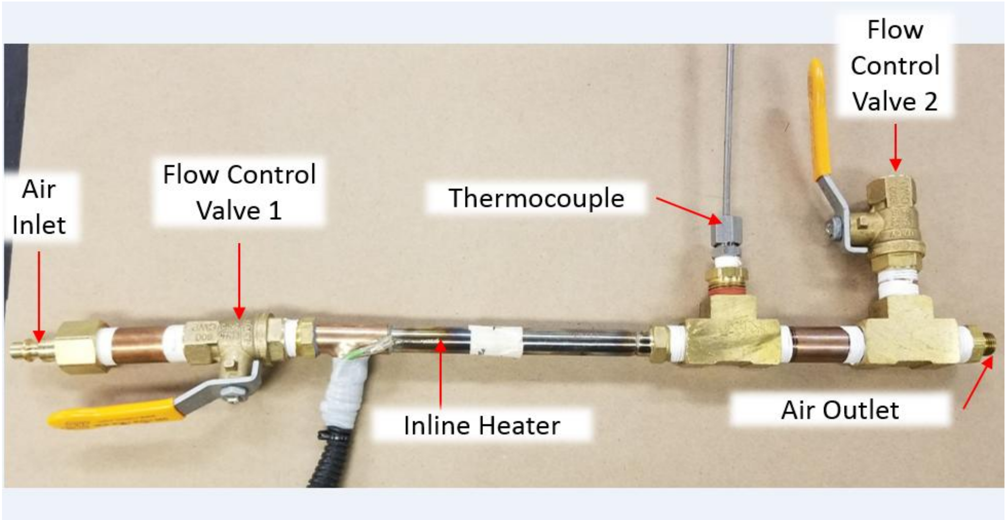


Figure 4: Inline heater placement on compressed air line to initiate hot air flush.

Residual metal was found in all of the channels after flushing with air, whether hot or cold. Flushing with chemical etchants was completed with various concentrations of HCl, $FeCl_3$, and NH_4OH solutions to remove the remaining residual sacrificial material from the walls of the channels after the initial melt-air blow out. A peristaltic pump was used to continuously flow the chemical etchant fluid through the channels. In some cases, the fluids were pre-heated from the reservoir using a heating mantel to assist with reaction kinetics to etch the metal alloy from the composite walls as efficiently as possible.

Results and Discussion

Placement of Sacrificial Materials

The quality of the channels was directly impacted by the placement of the sacrificial materials in the layup of the fabric. The placement of the wire between the second and third fabric layers or within the third layer resulted in rounder channels compared to placing the channels at the surface (Figure 5). When placed on top of the fifth layer of fabric, the metal wire was clearly flattened against the mold. Slight waviness along the channel can be noticed in cross sectional images resulting from the placement of the wire within the fabric. This is caused by the propensity of the channel to follow the topology of the fabric in the consolidated layups. Braiding of the wire into the fabric resulted in identical channel topologies to laying by hand, but was much less labor intensive to produce.

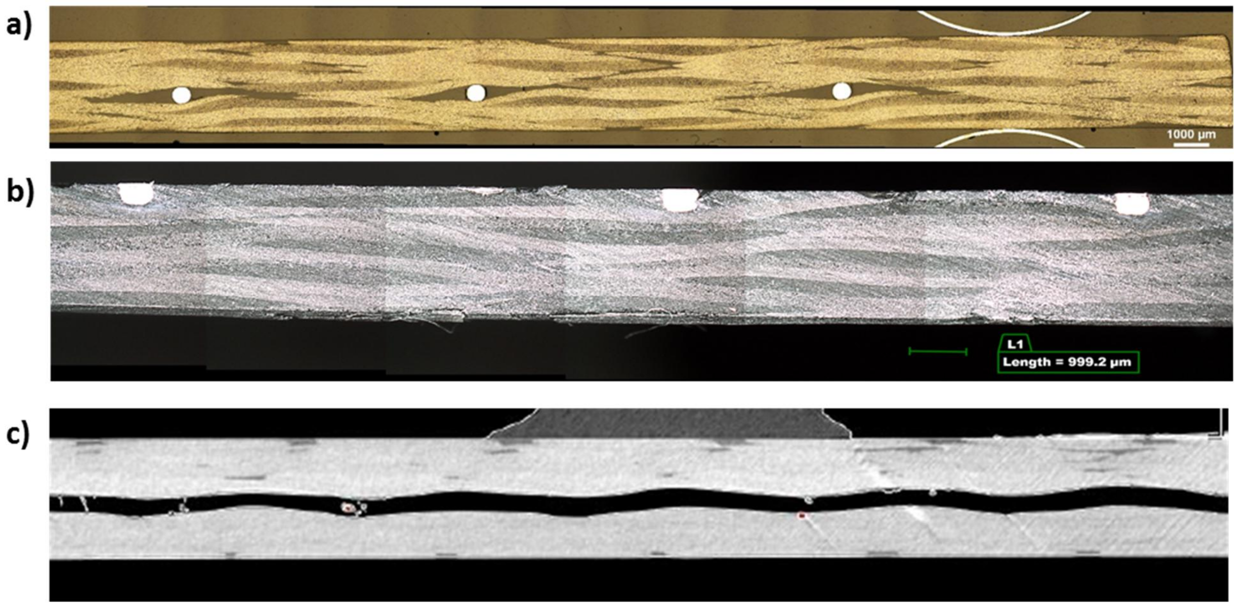


Figure 5: Wire placed by hand within the composite. (a) Circular wire resulting by placement between the second and third layer imaged before wire removal via optical microscopy. (b) Flattened/squished wire resulting by placement at the surface imaged before wire removal via optical microscopy. (c) Cross-sectional CT scan of wavy channel resulting by placement between the second and third layer.

Removing the Sacrificial Material

A variety of methods were trialed for removing the sacrificial material from the PMC to form clear channels. After fabricating the PMC with the wire preformed embedded, the bulk of the sacrificial material was removed by briefly heating the specimens to 205 °C, slightly above the melting point of the sacrificial material, and displacing the molten metal using house compressed air. Air at ambient temperature (*ca.* 22 °C) versus air at an elevated temperature (>200 °C) were compared. Initial visual results indicated that the elevated temperature air flush was more effective at removing the metal with minimal residual material, which was further confirmed by X-ray computed tomography (CT) with the Phoenix CT X-Ray System shown in Figure 6. CT scans were found to be effective for examining the interior of the channels for residual metal material without destroying the bulk sample. 2-D x-ray images were taken using the 240kV MF X-ray tube at a setting of 180 kV/180 µA.

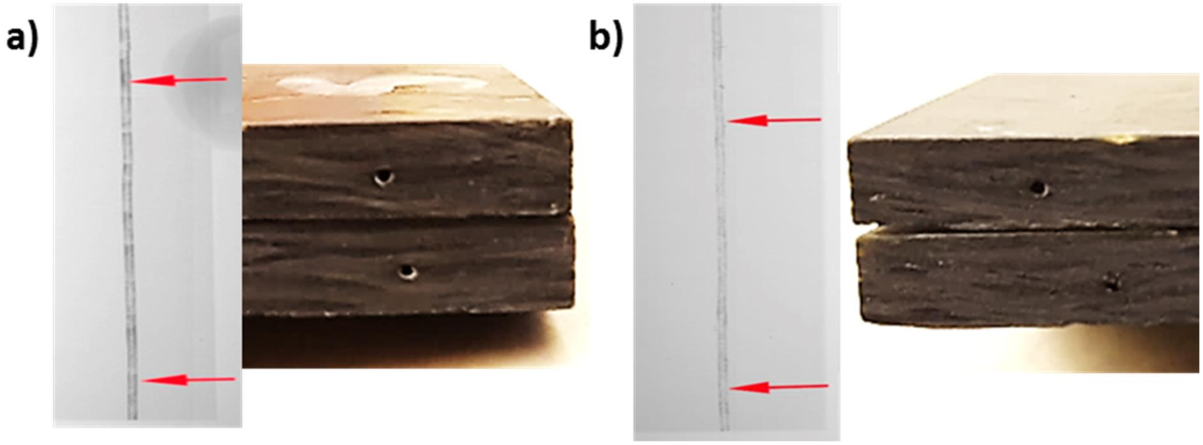
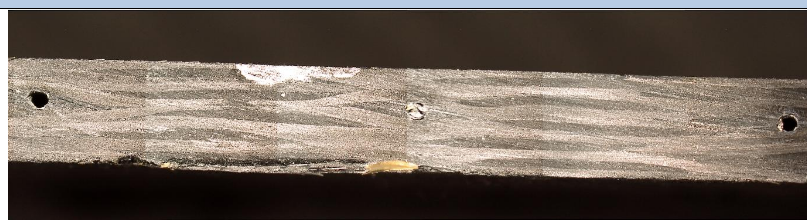
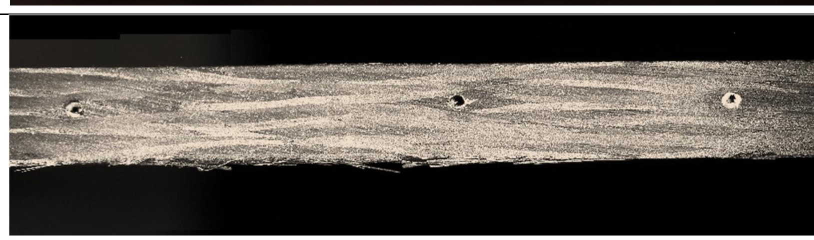
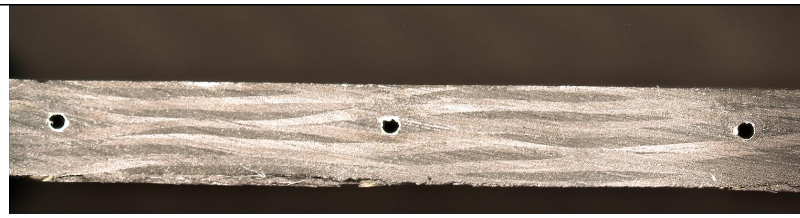
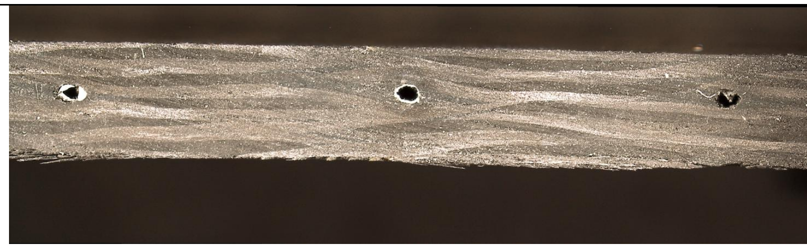
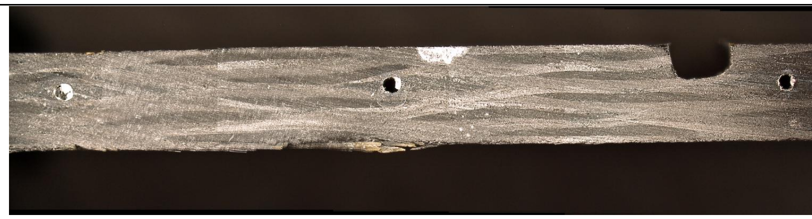
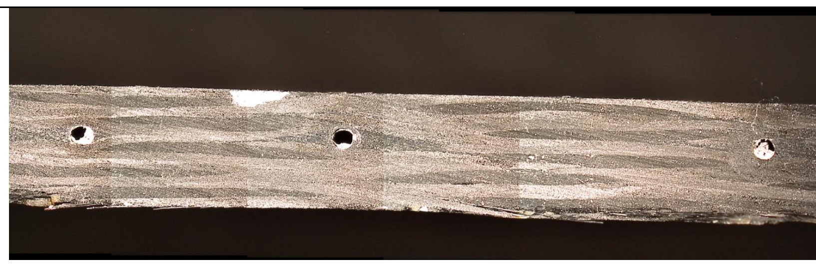
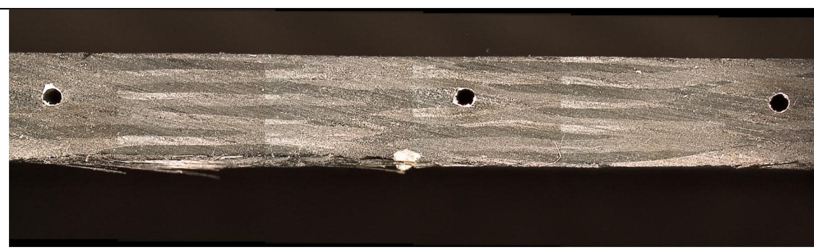


Figure 6: Compressed air flushing at 40 psi static pressure. (a) Room temperature air. (b) Elevated temperature air. Darker areas indicate the presence of residual metal. Red arrows indicate the location of the channel.

After removing the bulk of the sacrificial material from the channels, residual material could be seen left behind on the channel walls as illustrated in the CT scans in Figure 6. The residual material has the potential to flake off and cause blockages when the component is in use. An initial method trialed for prevention of residual material build up on the walls of the channel was to pre-coat the sacrificial material with various non-wetting release agents (higher temperature resistant sprays/polymer coatings). A list of the coatings can be found in Table 1. Visually, these methods appeared to produce a similar result to the non-coated sample, still maintaining a significant amount of residue left on the channel walls after being cut down the center to expose the circular channel openings.

Table 1: Methods of preventing residual material build up involving pre-coating the sacrificial materials before molding and preforming an ambient air flush: (a) Frekote 700, (b) Johnsons Paste Wax, (c) Meguiar's Mirror Glaze, (d) Vacuum Grease, (e) Ultra, (f) No Coating, (g)Wd40, (h) LPS1 Greaseless Lubricant.

Pre-Coating Type	Center Cut Channel Image
a) Frekote 700	
b) Johnsons Paste Wax	

c) Meguiar's Mirror Glaze	
d) Vacuum Grease	
e) Ultra	
f) No Coating	
g) Wd40	
h) LPS 1 Greaseless Lubricant	

X-ray fluorescence (XRF) was also performed on a small portion of the pre-coated samples. Similar to CT scans, XRF is a non-destructive technique that provides a semi-quantitative analytical comparison. Map scans were collected using the Bruker M-4 Tornado set at 40 kV/400 µA. Figure 7 illustrates the intensity contrast of elemental tin contained in each channel with red being the highest concentration and dark blue being lowest. There are three channels per sample, some channels appear to have less tin than others. The methods which involved Frekote 700 and Vacuum Grease appeared to show the highest concentrations of tin followed closely by the control non-coated sample. The XRF images showed Johnsons Paste Wax, Miguiar's Mirror Glaze, Ultra, Wd40, and LPS1 Greasless Lubricant had the greatest effect as a pre-coating material. However, the differences are minimal.

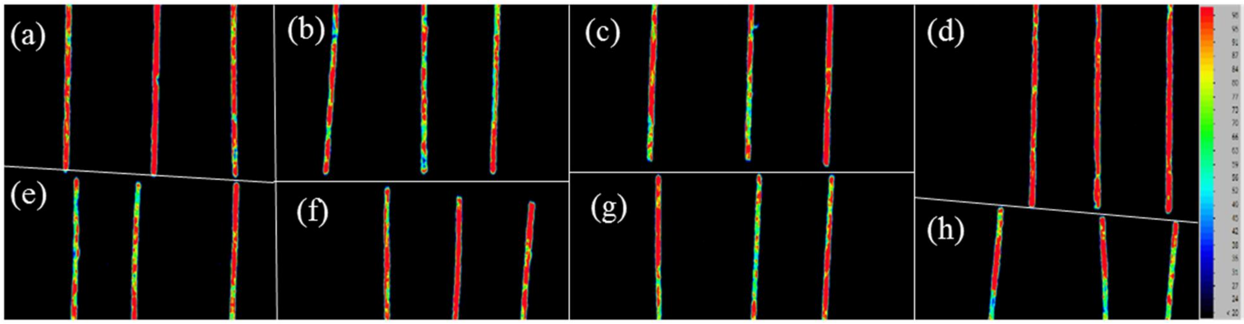


Figure 7: XRF images of intensity of elemental tin leftover after ambient air flush of pre-coated sacrificial materials: (a) Frekote 700, (b) Johnsons Paste Wax, (c) Meguiar's Mirror Glaze, (d) Vacuum Grease, (e) Ultra, (f) No Coating, (g)Wd40, (h) LPS1 Greaseless Lubricant.

A thick line scan was conducted across all samples shown in Figure 7 to confirm that the intensity differences or relative tin concentrations were minimal (Figure 8). Based on the intensity profiles of tin (green) shown in Figure 8, it appears that pre-coating the sacrificial material before molding does not make a significant impact. All counts averaged around the same as the control sample (f) with no coating.

After air flushing, since some residual material could still be seen left inside the channels, residual sacrificial material removal approaches were investigated and have been noted in Table 2 below with a star rating, five being the best preforming and zero being the control sample without air flush. The ratings were determined subjectively after visual inspection as well as through CT scan data shown in Figure 9 and Figure 10. The liquid chemical solutions have different reactive properties with the sacrificial Sn-Zn metal alloy that was selected. They act as an etching solution.

Concerning the etching solutions, HCl is known to produce a metal chloride and hydrogen in the presence of metals (Equation 1); a 75% solution was utilized in this study. NH_4OH will produce ammonia, a metal hydroxide and hydrogen (Equation 2); a 50% solution was utilized in this study. The reaction with $FeCl_3$ and Sn-Zn is known to produce a metal chloride and iron (Equation 3); a 2.5:100 parts by weight solution of this material was developed for this study. At the selected concentrations over various time periods each solution performed differently.

<u>Equation 1:</u> $Sn + HCl \rightarrow SnCl_2 + H_2$
$Zn + HCl \rightarrow ZnCl_2 + H_2$

<u>Equation 2:</u> $Sn + NH_4OH = NH_3 + Sn(OH)_4 + H$
$Zn + NH_4OH = Zn(OH)_2 + NH_3 + H_2$

<u>Equation 3:</u> $Sn + FeCl_3 = SnCl_2 + Fe$
$Zn + FeCl_3 = ZnCl_2 + Fe$

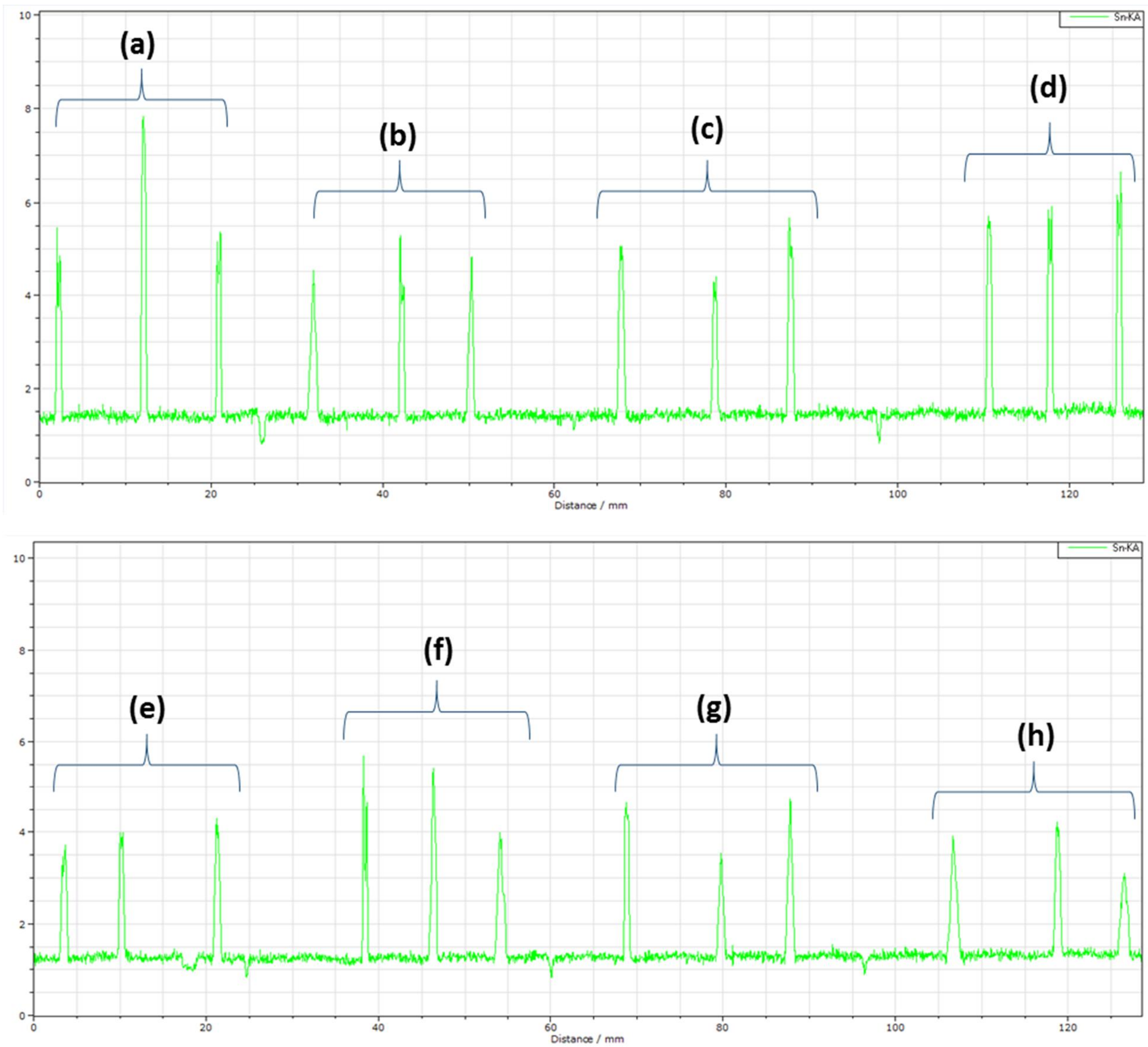
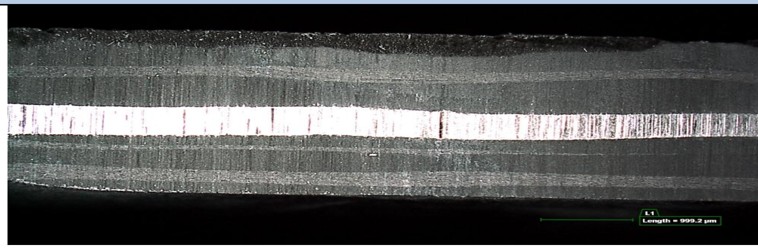
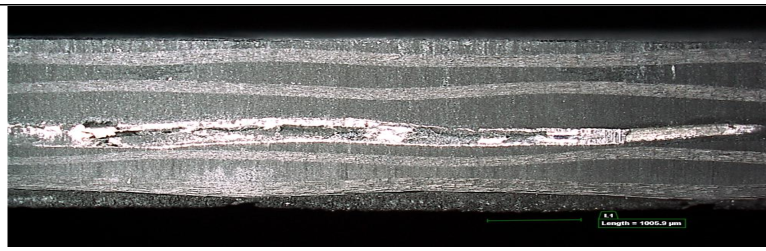
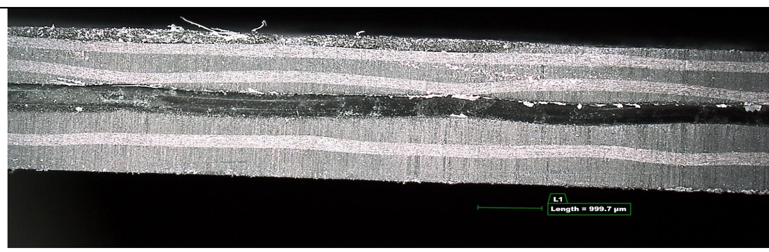
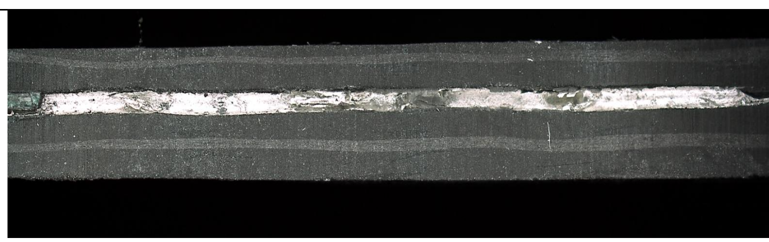
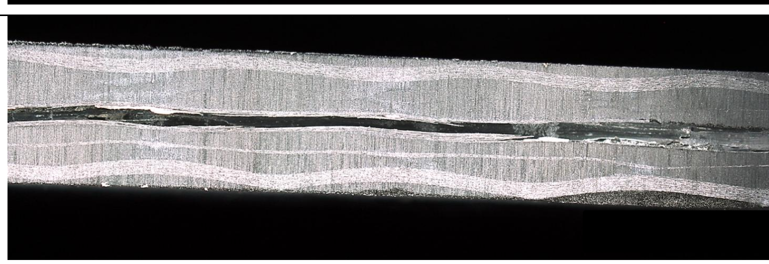


Figure 8: Nominal comparison of elemental tin (green) leftover per channel after ambient air flush of pre-coated sacrificial materials: *(a) Frekote 700, (b) Johnsons Paste Wax, (c) Meguiar's Mirror Glaze, (d) Vacuum Grease, (e) Ultra, (f) No Coating, (g)Wd40, (h) LPS1 Greaseless Lubricant.*

Table 2: Residual sacrificial material removal methods via liquid channel flushing.

Method	**Cross Sectional Image**	**Effectiveness (Out of 5 Stars)**
Control		-
Ambient Air Flush		★★
HCl Solution (75% by vol)		★★★★
NH_4OH (50% by vol)		★
$FeCl_3$ (2.5:100 parts by mass)		★★★★★

X-ray computed tomography was performed on several flushed samples over different periods of time (Figure 9). Results indicated the necessity for further treatment after the initial ambient air flush. There appears to have been a blockage in the left-most channel in Figure 9b most likely preventing fluid flow to that area. The second and third channels on that sample appear open but still contain more residual sacrificial material than the final HCl solution flushed sample in Figure 9c.

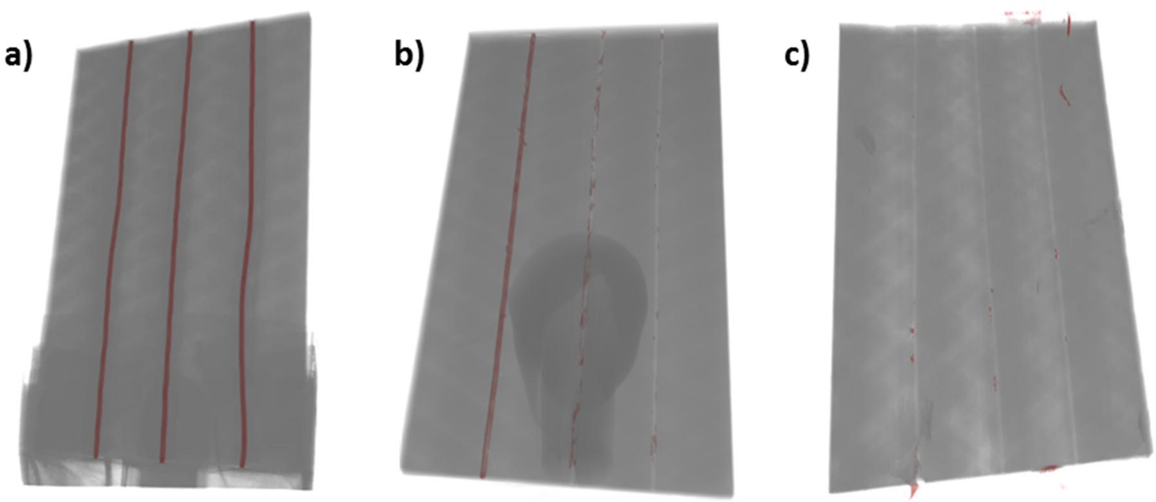


Figure 9: X-ray CT scan images of samples containing channels, red marking the presence of residual sacrificial material. (a) Ambient temperature air flush only. (b) 75% HCl acid solution flush at ~70 °C for 10min. Note: There was a blockage in the first channel after the air flush and the solution was unable to flow through it. (c) 75% HCl solution flush at ~70 °C for 30min. Red indicates the presence of residual metal.

Further investigation to examine the impact on higher temperature air treatment followed by etching was completed and samples were submitted for CT scan. Compared to the ambient air temperature flush followed by the etching treatment, the higher temperature air flush exhibited clearer channel pathways. Figure 10a and 10b were treated with hot and ambient air followed by HCl solution and Figure 10c and 10d were treated with both hot and ambient air followed by $FeCl_3$ solution. Visually the $FeCl_3$ solution appears to have a greater etching impact overall regardless of air temperature treatment leaving barely any trace of residue in the channels.

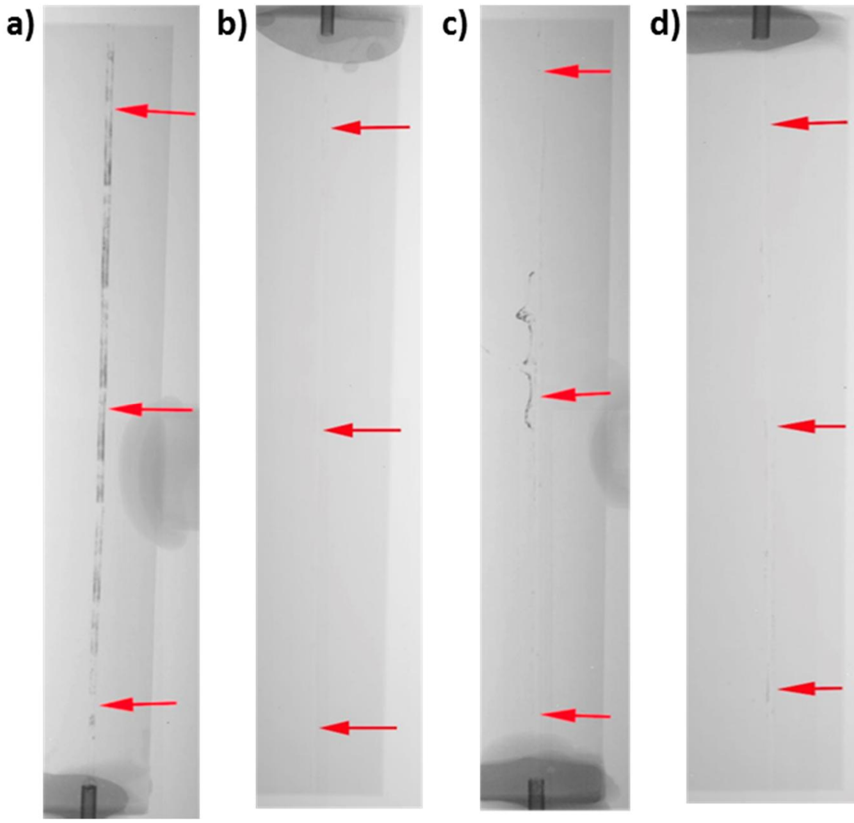


Figure 10: X-ray CT scan images of samples containing channels flushed with air followed by acid at 70 °C for 15 min each. (a) Ambient temperature air flush followed by HCl solution flushing. (b) Higher temperature air flush followed by HCl solution flushing. (c) Ambient temperature air flush followed by $FeCl_3$ solution flushing. (d) Higher temperature air flush followed by $FeCl_3$ solution flushing. Darker areas indicate the presence of residual metal. Red arrows indicate the location of the channel.

Mechanical Performance

Compression testing was performed to assess the effect of the channels on the mechanical performance of the composite. Data in Figure 11 below illustrates the differences in strength of composite plaques both with and without channels. Channels were formed with ambient air flush only and tested at two different temperatures, 23 °C and 120 °C. Strength was reduced at 120 °C, compared to 23 °C, due to the softening of the epoxy matrix at elevated temperature. However, no effect outside of the error bounds was observed as a result of the presence of the channels. Overall the modulus of the samples remained relatively constant with and without channels and at both temperatures.

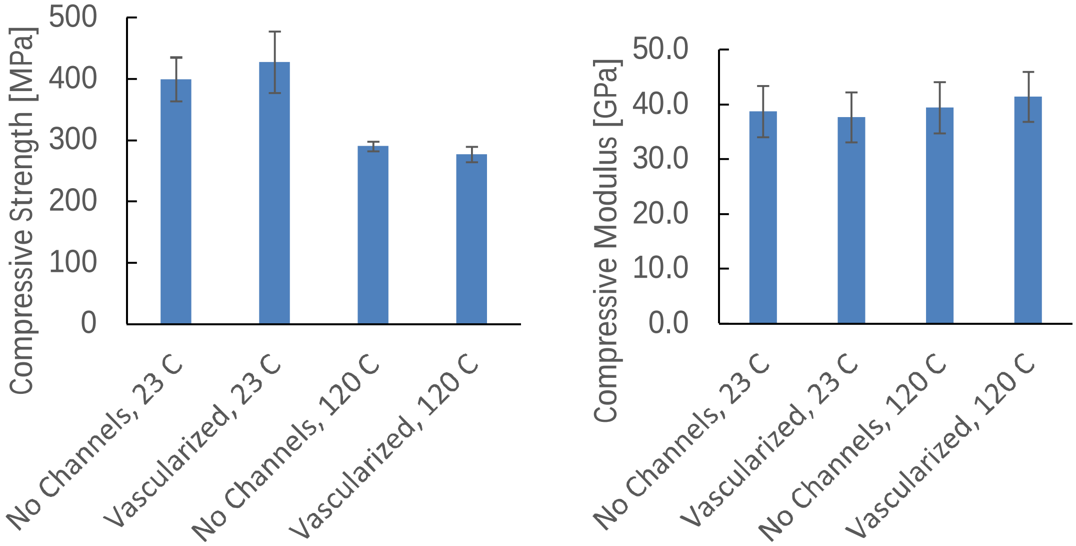


Figure 11: Mechanical stability data collected on samples with and without channels at 23 °C and 120 °C.

Conclusions

1. Flushing with air at a temperature above the melting point of the sacrificial material (>200 °C) was more effective than ambient temperature (*ca.* 22 °C) air flushing in removing the bulk sacrificial material but still left some residual metal material on the channel walls.
2. Chemical etching with $FeCl_3$ solution or HCl solution was effective in removing residual sacrificial material from the air flushed channels. CT scans of the materials indicated <1% residual material was left behind. The most effective treatment condition was determined to be with the $FeCl_3$ solution over a period of at least 15 min with a solution reservoir temperature of 70 °C.
3. The composite was chemically stable when subjected to etching treatments and there was no visible breakdown of the composite given the evaluated exposure conditions. CT scans of the materials indicated no major physical defects.
4. The mechanical performance of the composite was unaffected by the presence of the channels when tested in compression at both ambient (20 °C) and elevated temperature (120 °C) conditions.

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